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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 5/18, B65D 65/46, C08L 33/06		A1	(11) International Publication Number: WO 97/00282 (43) International Publication Date: 3 January 1997 (03.01.97)
<p>(21) International Application Number: PCT/GB96/01264</p> <p>(22) International Filing Date: 24 May 1996 (24.05.96)</p> <p>(30) Priority Data: 9512153.9 15 June 1995 (15.06.95) GB</p> <p>(71) Applicants (<i>for all designated States except US</i>): ZENECA RESINS B.V. [NL/NL]; Sluisweg 12, P.O. Box 123, NL-5140 AC Waalwijk (NL). ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): HEUTS, Martinus, Petrus, Josef [NL/US]; 20 Hawthorne Place, North Andover, MA 01845 (US). PADGET, John, Christopher [GB/GB]; 21 Fieldway, Frodsham, Cheshire WA6 6RO (GB).</p> <p>(74) Agents: SELLER, Alan; Zeneca Specialties, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB) et al.</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: WATER-SOLUBLE FILMS</p> <p>(57) Abstract</p> <p>Water-soluble film, suitable for sachets, comprised of a combination of soft and hard acid-functional polymers having Tg's of ≤ 20 and ≥ 40 °C respectively, the polymers being at least partially neutralised and present in a weight ratio (soft to hard polymer) within the range 90/10 to 65/35. Sachets made from the film are particularly suitable for packaging agrochemical and laundry care compositions.</p>			

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WATER-SOLUBLE FILMS

The present invention relates to a (preferably cold) water-soluble film suitable for the enveloping material of a sachet, to a certain polymer combination suitable for the provision of such a film, to an aqueous polymer composition comprising such a polymer combination, to a sachet in which the enveloping material comprises such a film, and to the use of such a sachet for packaging materials such as agrochemicals, laundry care materials, laundry items, dyestuffs, biocides, industrial or home surface cleaners and public health products.

Water-soluble sachets have utility for packaging a range of materials, usually formulated compositions, and particularly formulated compositions which are hazardous (or at any rate unpleasant) to individuals with whom they come into contact or are hazardous or harmful to the environment. Important examples include agrochemicals compositions (e.g. insecticides, herbicides, pesticides and fungicides), laundry care products (e.g detergents, fabric softeners and bleaches), laundry items themselves, dyestuffs, biocides, industrial or home cleaners, and public health products. The use of water- soluble sachets for packaging certain formulated compositions also provides a convenient way of adding a measured dosage of the formulation for subsequent dilution with water in order to provide the desired final concentration of the diluted formulation.

Agrochemical compositions can be packaged in water-soluble sachets, in which form they can be safely handled. The water-soluble sachet can be subsequently added to a spray tank containing water, and after dissolution of the sachet, the diluted formulation can be sprayed by the user, e.g. by a farmer. Complete dissolution of the sachet is normally necessary to avoid blockages during the spraying operation. It is therefore usually desirable that the film is cold water-soluble since it would be difficult to employ hot water in large scale outdoor use. Cold water- soluble means herein soluble in water at temperatures $\leq 35^{\circ}\text{C}$, and generally between 5 and 35°C .

The agrochemical composition is often a plant protection agent such as an insecticide, herbicide, fungicide, acaricide or nematocide. Combinations of two or more such compositions may be packaged together using two or more water-soluble sachets. For example, one sachet, containing an agrochemical composition, may also contain another water-soluble sachet itself containing a different agrochemical composition ("bag-in-bag" arrangement), so that, until use, the two agrochemical compositions remain entirely separate, but are both released when combined with water. Another combination arrangement has two (or more) sachets, with different compositions packaged therein, joined together edgewise (e.g. with a thin strip of the film material) ("side-by-side" arrangement), both compositions again being released on combination with water. Less usually, two or more compositions may be packaged together in the same sachet if desired and feasible; however, this is not common because of problems of unwanted cross contamination between the compositions. In general the agrochemical

composition in a sachet comprises the active ingredient(s), in association with other ingredients such as surfactants, thickeners, antifoaming agents, gelling additives, dispersants and antifreezes.

5 The agrochemical composition can be in the form of a solid (e.g. powder, granules) or a liquid (e.g. a non aqueous solution, a non aqueous dispersion, an aqueous solution or an aqueous dispersion). The viscosity of liquid agrochemical compositions can be varied to provide a thickened liquid or a gel depending on the rheological properties required. Viscosification or gellation reduces the risk of both leakage through pinholes in the sachet walls and spillages in the event of a sachet being damaged.

10 Polyvinyl alcohol (PVA) is widely utilised for the preparation of water dissolvable film for the production of sachets for packaging hazardous materials such as agrochemicals; polyethylene oxide and methyl cellulose are also widely utilised (see e.g. WO 93/22215). Such polymers however have limitations. For example, the films tend to be blocky when damp. In addition it is frequently necessary to incorporate plasticizers to 15 achieve the desired level of flexibility; plasticizers can migrate out of the film to render it brittle and can further increase the risk of blocking.

20 In the realm of laundry care, it has been a continuing objective to provide a convenient means for adding discrete, usually premeasured, quantities of laundry care materials (e.g. cleansing substances or cleansing auxiliaries) to the aqueous wash medium. Coupled with this objective is the cognizance that many laundry care materials in common use are detrimental to the user's skin; examples of such materials are 25 bleaches, detergents, fabric softeners and conditioners, and enzymes. It is therefore known to be desirable to add such laundry care materials to the wash medium without them coming into contact with the skin of the user.

30 25 It is known to achieve both objectives by the use of water-soluble laundry care sachets - alternatively called laundry care bags, pouches, seals, packages or envelopes. In such sachets, the laundry care material is enveloped by a film material which dissolves in the aqueous wash medium after addition thereto, thereby releasing the laundry care material. It is therefore possible with such sachets to add discrete doses of laundry care materials to a wash medium, as for example in a washing machine, without any contact with the user's skin, and to arrange for the dose to be of an amount sufficient for a single wash.

35 It is, furthermore, possible for the packaged material to be the laundry itself (e.g. linen items). Thus, water-soluble laundry care bags may be used for the collection of contaminated laundry items (e.g. from hospitals, chemical laboratories or plants etc) whereby the bag and its contents may be placed in a washing machine without the requirement for additional handling of the laundry. The bag then dissolves in the wash cycle water to release the contaminated laundry.

Various water-soluble film materials suitable for sachets of the type discussed above have been proposed in the prior art, but have not proved to be entirely satisfactory for one reason or another.

For example, in US Patent 4747976 it is proposed to use as the enveloping material for laundry sachets a water-soluble film which predominantly comprises the water-soluble polymer polyvinyl alcohol (PVA). A drawback with PVA (in addition to those mentioned above when discussing the use of PVA for providing sachets for packaging agrochemicals) is that it interacts with borates (a common component of washing detergents) to form insoluble gelled material which can form an undesirable deposit on the items being washed. The teaching of US 4747976 to overcome this problem is to use borate scavengers; however these scavengers may tend to remove some of an important bleaching component of the detergent formulation, i.e. the borates, thereby rendering the detergent less effective. They will also add to the cost of these types of sachets.

Another type of laundry care sachet is disclosed in European Patent Application EP-A-217186 and US-A-4654395, this being a sheet laminate in which two films of a water-soluble addition polymer (usually acrylic in character) are sealed together so as to incorporate a thin layer of laundry care additive, whereby during sealing the polymer sheet softens and flows at least in part into the interstices or voids between the additive particles. The water-soluble addition polymer of this type of sachet in EP-A-217186 is formed from about 0 to 85 weight % of a water-insoluble soft monomer, 15 to 100 weight % of a water-soluble anionic monomer (such as acrylic acid or methacrylic acid), 0 to 25 weight % of a water-soluble nonionic monomer, and 0 to 40 weight % of a water-soluble hard monomer, and where the polymer is up to 100% neutralised with a Group IA metal base or a Group IA metal basic salt. In US-A-4654395 such a sachet is formed from about 40 to 95 weight % of a water-insoluble soft monomer, 3 to 15 weight % of a water-soluble anionic monomer, 0 to 25 weight % of a water-soluble nonionic monomer, and 0 to 40 weight % of a water-soluble hard monomer, and where the polymer is at least 75% neutralised with a Group 1A metal base or a Group 1A metal basic salt. (The terms "soft", "hard", "water-soluble", and "water-insoluble" as used in EP-A-217186 and US-A-4654395 are presumed to relate to the monomers in question when in their homopolymerised state).

The presence of the neutralised anionic monomer repeat units in the polymer of EP-A-217186 or US-A-4654395 provides the necessary water-solubility of the sheet material (optionally in conjunction with units of water-soluble nonionic monomer), while the presence of the repeat units of soft monomer is said to provide flexibility in the sheet material enabling it to withstand handling without premature rupture or disintegration, while the presence of the repeat units of the hard monomer is said to reduce the tack of the sheet at high relative humidity, although substantial amounts must be avoided else low temperature flexibility of the sheet is reduced.

It is also specified in EP-A-217186 and US-A-4654395 that, in general, at least about 40 weight % of the soft monomer should be employed in order to impart sufficient low temperature flexibility to the polymer sheet; alternatively it may be possible to employ less than 40% soft monomer, but in that event plasticisers are often required to provide needed flexibility to the sheet. However, in our experience, both of these expedients have their drawbacks. Thus a polymer film having a very high level of soft monomer repeat units tends to be tacky, so that sheets of the free film (prior to sachet formation) when stacked or rolled on a reel for storage or transport may stick together in an unacceptable fashion (this drawback being known as "blocking"); similarly, packed sachets made from this type of film may stick together (block) after prolonged storage. On the other hand, polymer films with lower levels of soft monomer repeat units but needing to incorporate plasticiser to maintain sufficient flexibility also have drawbacks, these being associated with the actual requirement to use plasticiser. Thus, such plasticisers must be water-soluble so that only a limited number of compounds can be employed. The preferred plasticiser compounds would be materials such as glycol and glycerol (including water-soluble plasticiser derivatives thereof such as glyceryl triacetate); a less preferred plasticiser compound would be low molecular weight polyethylene glycol (PEG). However, compounds like glycol and glycerol are very mobile and may migrate out of the film (into the packaged materials) so as to render it brittle. The migration of such compounds may also cause blocking of the sachets or blocking of stacked sheets or rolls of free film. High relative humidities might be expected to make this problem worse. PEG types of plasticisers are less effective (on a weight % basis) and tend to unacceptably slow down the water dissolution of the film.

We have now discovered how to overcome possible problems of the type discussed in the preceding paragraphs and have invented water soluble, substantially or wholly plasticiser-free (i.e. totally or very nearly free of external plasticiser) films having both excellent flexibility appropriate to their use for sachets and excellent non-blocking characteristics. Such sachets are eminently suitable for packaging applications of the type discussed above in the introduction of this specification.

According to the present invention there is provided a flexible water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film suitable for the enveloping material of a sachet, said film being comprised of a combination of the following polymer components S and H in which :

S is defined as at least one acid-functional olefinic addition copolymer which is soft in character by virtue of having a $T_g \leq 20^\circ\text{C}$, and
H is defined as at least one acid-functional olefinic addition copolymer which is hard in character by virtue of having a $T_g \geq 40^\circ\text{C}$,
and wherein further the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35 and the acid-functionalities of S and H are at least partly neutralised such as to render the film water-soluble.

There is further provided according to the invention a polymer combination suitable for the provision of a flexible, water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film which is itself suitable for the provision of the enveloping material of a sachet, said polymer combination comprising a combination of the polymer components S and H, where S and H are as defined above, and wherein the components S and H are present in a weight ratio of from 90/10 to 65/35, and the acid-functionalities of S and H are either at least partly neutralised such as to render a film made from the polymer combination water-soluble, or are unneutralised or insufficiently neutralised to render a film made from the polymer combination water-soluble but are capable of being so at least partly neutralised such as to render a film made from the polymer combination water-soluble.

By the Tg of a copolymer herein is meant the glass transition temperature of the copolymer; as is well known, the Tg of a polymer is the temperature at which it changes from a glassy, brittle state to a plastic, rubbery state. Tg may be determined experimentally, e.g by using differential scanning calorimetry (DSC), taking the peak of the derivative curve as Tg, or calculated from the Fox equation, whereby the Tg (in degrees Kelvin) of a copolymer having "n" copolymerised comonomers is given by the weight fractions W of each comonomer type and the Tg's of the homopolymers (in degrees Kelvin) derived from each comonomer according to the equation :

20

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} + \dots + \frac{W_n}{Tg_n}$$

The calculated Tg in degrees Kelvin may be readily converted to °C. (For the sake of clarity, the Tg's herein of soft and hard copolymers are intended to be those Tg's of the copolymers prior to any neutralisation).

It is thus found that the water-soluble film of the present invention possesses excellent flexibility suitable for sachets as well as lack of tackiness for imparting good non-blocking behaviour, even though an individual copolymer component thereof, namely S, necessarily contains high levels of soft monomer repeat units and the film is free (or substantially free) of plasticising material. (If present the amount of plasticiser is usually <15 %, more usually <4%, and still more usually <2%, based on total polymer weight, although most usually, none is present).

There is also provided according to the invention a sachet in which the enveloping film of the sachet comprises a film as defined supra. Preferably, the material packaged in the sachet is an agrochemical or laundry care composition, although it can also be e.g. a dyestuff composition, a laundry item(s), a biocide composition, an industrial or home surface cleaning composition, or a public health product.

There is further provided according to the invention the use of a sachet as defined supra for packaging a material, preferably an agrochemical material, a laundry care material, a dyestuff, a laundry item(s), a biocide, an industrial or home surface cleaner, or a public health product.

5 It is to be understood that the various variations regarding the packaged compositions and sachet arrangements, discussed in the introduction of the specification, are intended to be applicable to the present invention.

10 By an olefinic addition copolymer is meant herein a copolymer derived from the addition copolymerisation, usually free-radical initiated, of olefinically unsaturated monomers. Usually the olefinic addition copolymers of both S and H are acrylic polymers in that they will be derived from monomers which are predominantly (>50 mole %, usually >80 mole % of the monomers used for the copolymerisation) acrylic in nature by virtue of having the formula $\text{CH}_2=\text{CHR}^1\text{-C(=O)}\text{XR}^2$ where R^1 is H or methyl, R^2 is alkyl usually of 1 to 18 carbon atoms (more usually 1 to 8 carbon atoms), cycloalkyl usually of 5 to 12 ring carbon atoms (more usually 5 or 6) or H, and X is -O- or -NH-.

15 Each copolymer of type S and type H will be derived from olefinically unsaturated monomers which comprise at least one acid-functional olefinically unsaturated monomer for imparting, after at least part neutralisation when incorporated in the copolymer, water-solubility to the film material. Examples of such acid-functional monomers include 20 olefinically unsaturated monomers having acid groups such as carboxylic acid and sulphonic acid; also included in this type of monomer grouping are monomers which could yield, after suitable treatment of the copolymer, acid-functional groups, and examples of these are acid amides, acid chlorides, acid anhydrides and nitriles. More 25 specifically, monomers containing carboxylic acid groups are preferred and examples of these include acrylic acid, methacrylic acid, beta-carboxy-ethylacrylate, itaconic acid, maleic acid and fumaric acid. Particularly preferred are acrylic acid and methacrylic acid.

30 The amount of the at least one acid functional monomer (or rather the polymerised units therefrom) in each copolymer type S and H should be sufficient to impart the desired water-solubility, preferably cold water-solubility, in the film as a whole, but should not be so high as to preclude the sufficient presence of units of other monomers which impart the desired characteristics of hardness and softness. (As mentioned above, cold water solubility herein means that the film is soluble in water at temperatures $\leq 35^\circ\text{C}$, and generally within the range of from 5 to 35°C). (Note that if the film is cold water-soluble, it will also, in virtually all cases, be hot water-soluble as well, i.e. soluble at water temperatures $> 35^\circ\text{C}$ - e.g. up to 70°C and above). Generally 35 speaking the monomers used to form each polymer type S and H will have a level of acid-functional monomer which is in the range of from 5 to 40 weight % of the monomers used. A preferred range, however, is 8 to 15 weight %, and more particularly 8 to 14 weight %. (Typical values would be 11 and 12 weight %). It should also be borne in 40 mind that while a copolymer could be water-soluble, its actual dissolution rate in water

could vary according to the level and type of acid-functional monomer in the copolymer and to the hydrophilicity of the non-acid functional comonomer(s). The solubility could also be influenced by the presence of other water-soluble polymer(s) in the film. For example if a water-soluble copolymer with a very high dissolution rate were present in the film together with a copolymer of a water-soluble copolymer with, if it were considered in isolation, a relatively much slower dissolution rate, the dissolution rate of the latter is found to be significantly increased. This effect is enhanced when the slower dissolving copolymer is present in a minor amount compared to the faster dissolving copolymer (e.g. <50 weight % based on the weight of slower plus faster dissolving copolymers).

As specified supra, the acid-functional groups in each copolymer of type S and H in the invention film should be at least partially neutralised in the copolymer (before, or more usually, after formation of the copolymer). Preferably 50 to 100%, more preferably 80 to 100% (and more often 100%) of the acid groups should be neutralised. This will provide acid group anions (e.g. $-CO_2^-$) in the copolymer for imparting water-solubility.

It will also, in principle, be possible to use small amounts of hydrophilic non-acid-functional monomers for making polymers of type S and H, in addition to the acid-functional monomers to further enhance water-solubility (say 0 to 10 weight %); examples include C1 to C6 hydroxyalkyl acrylates or methacrylates such as hydroxyethyl acrylate, hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and 2-hydroxypropyl acrylate.

A copolymer of the type S will be made from an appropriate combination of monomers which will provide, in addition to the required water-solubility, a T_g of $\leq 20^\circ C$. Such monomers will include, in addition to acid-functional monomer(s), monomer(s) of the soft type (i.e. which when homopolymerised yield a polymer of low T_g , say $T_g < 0^\circ C$) and usually, to balance the desired physical properties of the copolymer, monomer(s) of the hard type (i.e. which when homopolymerised yield a polymer of high T_g , say $T_g > 20^\circ C$, often $> 60^\circ C$), although of course the level of soft monomer(s) in the monomer composition for polymerisation will predominate (and will usually be ≥ 40 weight %, more usually ≥ 50 weight %, and often ≥ 60 weight % of the monomers used).

Examples of suitable soft monomers include primary and secondary alkyl acrylates, in which the alkyl group has up to 18 or more carbon atoms, and primary and secondary alkyl methacrylates in which the alkyl group has 5 to 18 or more carbon atoms. Other soft olefinitely unsaturated monomers could also be used, examples of which include : olefin monomers, such as ethylene, propylene and isobutene, and conjugated dienes such as butadiene, chloroprene, and isoprene. Monomers containing polyoxyalkylene groups, such as methoxy-poly(ethylene glycol) methacrylate may also be used.

The preferred soft monomers include alkyl acrylates in which the alkyl group has from 1 to 8 carbon atoms and alkyl methacrylates wherein the alkyl group has from 5 to

18 carbon atoms. Examples of such compounds include : n-amyl acrylate; 2-ethylhexyl acrylate; n-octyl acrylate, n-amyl methacrylate; n-hexyl methacrylate; n-octyl methacrylate; n-dodecyl methacrylate and those acrylates or methacrylates with substituted alkyl groups, such as butoxyethyl acrylate or methacrylate. However, it is 5 especially preferred to employ alkyl acrylates in which the alkyl group has from 1 to 4 carbon atoms. Typical compounds include : methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate and n-butyl acrylate, and preferably ethyl acrylate and n-butyl acrylate.

10 Examples of suitable hard monomers include benzyl acrylate or methacrylate, vinyl chloride, chlorostyrene, vinyl acetate, acrylonitrile, methacrylonitrile, styrene and alpha-methyl styrene. However it is especially preferred to employ C₁ to C₄ alkyl methacrylates, examples of which include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and sec-butyl methacrylate. An especially preferred hard monomer is methyl methacrylate.

15 A copolymer of type S will often be derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid-functional monomer(s), soft monomer(s), and hard monomer(s) :

20 acid-functional monomer(s) : 5 to 40 wt. %, more usually 8 to 15 wt. %,
particularly 8 to 14 wt %.
soft monomer(s) : 40 to 85 wt. %, more usually 55 to 70 wt. %,
particularly 60 to 70 wt. %.
hard monomer(s) : 5 to 50 wt. %, more usually 15 to 35 wt. %,
particularly 20 to 30 wt. %.

25 (The above amounts of soft and hard monomers exclude acid-functional monomers whether hard or soft : these are included in the acid-functional monomer range).

30 Examples of monomers combinations for making the soft copolymers (using appropriate levels of soft and hard monomers) are : acrylic acid/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/methyl methacrylate; methacrylic acid/ethyl acrylate/n-butylacrylate/methyl methacrylate; acrylic acid/methacrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; and acrylic acid/methacrylic acid/ethyl acrylate/methyl methacrylate.

35 A copolymer of the type H will likewise be made from an appropriate combination of monomers which will provide, in addition to the required water-solubility, a T_g of \geq 40°C. Again such monomers will include, in addition to the acid-functional monomer(s), monomer(s) of the soft type (as described supra) and monomer(s) of the hard type (also as described supra), although in the case of a hard polymer type, the level of hard

monomer(s) used will now predominate (and will often be \geq 40 weight %, more usually \geq 50 weight % of the monomers employed for the polymerisation).

Examples of suitable soft and hard monomers for copolymers of type H are as described supra in respect of the soft and hard monomers for copolymers of type S.

5 A copolymer of type H will often be derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid functional monomer(s), soft monomer(s), and hard monomer(s) :

acid-functional monomer(s) : 5 to 40 wt. %, more usually 8 to 15 wt. %,
particularly 8 to 14 wt. %.

10 soft monomer(s) : 0 to 50 wt. %, more usually 10 to 40 wt. %,
particularly 25 to 40 wt. %.

hard monomer(s) : 40 to 90 wt. %, more usually 50 to 80 wt. %,
particularly 50 to 65 wt. %.

15 (The above levels of soft and hard monomers exclude acid-functional monomers whether hard or soft : these are included in the acid-functional monomer range).

15 Examples of monomers combinations for making the hard copolymers can be the same as those described supra for soft copolymers, but of course using different (i.e. appropriate) amounts of hard and soft monomers.

20 With further regard to the neutralisation of the acid-functional groups, the required degree of neutralisation can be brought about by the use of an appropriate base or basic salt so as to convert the desired proportion of acid-functional groups to anionic salt groups together with the corresponding presence of cations derived from the base or basic salt. Bases which could be used are non-volatile (i.e. permanent) bases such as the IA or Group II metal bases or basic salts, e.g. hydroxides, bicarbonates or 25 carbonates (as appropriate) and particularly the hydroxides of Na, K and Li, and non-volatile water-soluble organic bases such as triethanolamine and 2-methyl-2-amino-1-propanol. Volatile bases which could be used are ammonia and volatile aliphatic amines such as triethylamine, diethanolamine and the like. However, it is preferred in most cases to use non-volatile (i.e. permanent or fixed) bases (since volatile bases might be lost during film formation and storage of the films - leading to impaired water-solubility), with the most preferred permanent base being NaOH. Nevertheless, the use of volatile bases such as (in particular) ammonia may be advantageous in some cases.

30 The amount of base used may usefully in some circumstances be in excess of that required to neutralise all of the acid-functional groups in the copolymers of S and H, so that, in the case of using a permanent base, the resulting film contains residual base from the neutralisation. The presence of such residual base in the film can provide a greater rate of dissolution in water. The amount of non-volatile base from neutralisation remaining in the film in such an embodiment is preferably up to 20 wt %, based on the weight of the film.

As indicated supra the relative weight of polymer components S and H should be in the range of from 90/10 to 65/35. If the ratio of S/H is below 65/35 in the film, it tends to be too inflexible for use as a sachet; on the other hand if the ratio is above 90/10, the film tends to be tacky and incurs blocking problems. A more preferred range for S/H is 5 85/15 to 70/30.

The Tg of a soft copolymer (i.e. of type S) is, as indicated supra, $\leq 20^{\circ}\text{C}$. More preferably it is $\leq 10^{\circ}\text{C}$. A usual range for the Tg of a soft copolymer for use in the invention is -20 to 20°C , more usually -10 to 10°C , particularly -8 to 5°C .

10 The Tg of a hard copolymer (i.e. of type H) is, as indicated supra, $\geq 40^{\circ}\text{C}$. More preferably it is $\geq 50^{\circ}\text{C}$. A usual range for the Tg of a hard copolymer for use in the invention is 40 to 90°C , more usually 50 to 80°C , and particularly 50 to 70°C .

15 The molecular weights of the soft and hard polymers can have an influence on the dissolution rate in water of the film and also on the mechanical properties. Flexibility and maximum elongation tend to improve with increasing molecular weight. On the other hand, increasing molecular weight may tend to decrease the rate of water dissolution. Preferably the weight average molecular weight (Mw) of a soft polymer used in the invention is $\leq 300,000$, and a preferred range is 50,000 to 300,000, more preferably 50,000 to 200,000. The molecular weight of hard polymer for use in the invention is of 20 less influence on the resulting film properties, but its Mw will usually be within the range of from 10,000 to 500,000, more usually 30,000 to 200,000. (Polymer molecular weights may be readily determined e.g. by gel permeation chromatography calibrated using an appropriate known polymer as standard).

25 The hard and soft copolymers may be made using any suitable free radical polymerisation technique, such as emulsion polymerisation, suspension polymerisation, microsuspension polymerisation, solution polymerisation and bulk polymerisation. Photopolymerisation techniques could also be used in principle. The techniques for such polymerisation are very well known and understood by those skilled in the art and do not require any detailed explanation. It is preferred to employ aqueous emulsion polymerisation for making the copolymers, so that they are produced in aqueous latex 30 form. Such a technique, as mentioned, is very well known; suffice to say that the monomers are polymerised in the presence of an emulsifying agent (surfactant : can be anionic and/or nonionic type) in the presence of a suitable initiator system (e.g an alkali metal or NH_4 persulphate, or a peroxide such as t-butyl hydroperoxide; redox initiator systems can also be used) and at a suitable polymerisation temperature (typically 35 between about 30°C to about 100°C). Other components such as chain transfer agent (usually thio materials such as esters of mercaptoalkanoic acids) can also be used as appropriate.

40 In principle, any technique may be used to derive a film from the combination of hard or soft polymers, for example calendering, extrusion or, more preferably, by casting. When the film is to be made by casting, a solution or dispersion of the polymer

5 combination, together with any desired additive(s), is poured onto a suitable mould flat horizontal surface (e.g. made of a plastics material such as polyethylene or polypropylene) and solvent or continuous carrier phase removed by natural or accelerated evaporation (e.g. at room temperature or at an elevated temperature as for example in an oven). A film could also be made by coating onto a flat surface using an applicator bar to determine film thickness rather than mould dimensions.

10 In one preferred method of combining the soft and hard polymers for forming the film, there is formed an aqueous composition comprising an aqueous solution (or in some cases an aqueous latex) of the polymers of components S and H which has been derived from aqueous latices of the unneutralised polymers by the at least partial neutralisation thereof. This may be effected, for example, by separately forming aqueous latices of the unneutralised hard and soft copolymers, using aqueous emulsion polymerisation, and adding sufficient of a base (such as NaOH), and additional water if required, to obtain a clear aqueous solution (or in some cases an aqueous latex) of the copolymer, and then blending the aqueous solutions in the appropriate ratio to achieve a polymer solution from which films according to invention may be cast. It would also be possible to blend the soft and hard emulsion polymer latices (in the appropriate ratio) before neutralising with a base (and optionally adding more water if necessary). A further possibility would be to sequentially emulsion polymerise the monomers for the hard and soft copolymers (or vice versa) in the necessary phase ratios; the so-obtained emulsion polymer system could then be treated with base, and additional water if necessary without having to blend separate solutions or latices.

15 Therefore, there is further provided according to the invention an aqueous polymer composition suitable for the provision of a film (as defined supra) which composition comprises an aqueous solution or latex of the copolymers of components S and H as defined above which has been derived from aqueous latices of the unneutralised copolymers and wherein in said aqueous composition the acid-functionalities of S and H are either at least partly neutralised such as to render a film made from the aqueous polymer composition water-soluble, or are unneutralised or insufficiently neutralised to render a film made from the aqueous polymer composition water-soluble but are capable of being so at least partly neutralised such as to render a film made from the aqueous polymer composition water-soluble.

20 25 30 35 Generally speaking, the solids content of the final aqueous solution or latex in this embodiment will often be in the range of from 10 to 25 weight %, more usually 12 to 23 weight % (on a total weight basis).

40 Often, the enveloping film of the sachet will be of a monolayer structure and provided by a single (i.e. monolayer) film(s) according to the invention. However, it is within the scope of the invention for the sachet to be formed from a double layer (i.e. a laminated) film. Such laminate films can be formed by techniques such as sequential casting, co-extrusion, and lamination of two preformed films. The films of a laminate may

be of the same or different composition. One or both should of course be according to the invention, and if one is a non-invention film, it must have suitable properties for the sachet such as good water-solubility, heat sealability and so on. An example of a possible non-invention film for use in a laminate in some applications would be a PVA film. Another example would be a film having a composition as per the invention except that neutralisation has been effected with a volatile base (such as ammonia) which has been caused or allowed to become released on film formation so that the resulting film is inherently water-insoluble and so not according to the invention. Such a film would be useful for use in a laminate film sachet as the inner film directly contacting the packaged material, with the outer film of the sachet being a permanent base (e.g. NaOH) - neutralised film according to the invention which has excess residual base present therein as a result of using an excess of the permanent base over that needed for complete neutralisation. Such a sachet would be useful for packaging an aqueous-formulated material, since the inner film would prevent premature release of the contents prior to use (being water-insoluble); upon immersion of the sachet in water, however, the laminate film as a whole would become water-soluble by virtue of the transport of excess base from the outer film to the inner film (allowed by the uptake of water in the outer film) thereby rendering the latter water-soluble and so enabling the packaged material to be released.

The actual sachet containing its packaged material can be prepared using any suitable production technique. For example it may be made by simply first forming an unfilled sachet comprising the film walls joined or integrally formed together along their edges but leaving an opening along at least part of an edge, filling the sachet with the material(s) to be packaged and finally sealing up the opening. The unfilled sachet in such a method can be made e.g. from a single piece of film folded over and sealed along the two side walls so formed, or alternatively from two separate pieces of film which are sealed along their contacting edges except for a region which provides an opening. After filling with the material to be packaged, a suitable seal is then made between the edges of the film or films providing the opening so as to form the filled sachet. Preferably the seals in this method (and in other methods - see following) are made by heat sealing the walls together. The heat sealing can be carried out by standard methods such as compressing together the edge portions of the films to be sealed and heating them to, for example, about 130°C for a few seconds. Typically this forms a sealed border between 3 and 10mm wide around the edge of the sachet.

For more rapid, automated filled sachet production, a "vertical form-fill-seal" process may be used. In this method a single roll of film is fed over a series of support rollers and then wrapped around a former, which is referred to as the "shoulder". A hollow tube which runs through the middle of the former is used for filling with the product. As the film passes through the "shoulder" the sheet of film overlaps to form a tube which is heat sealed at the overlap by a vertical jaw. While held in place, the tube

passes through a heating jaw which clamps the film together and forms the top and bottom cross seals of the sachet. Prior to forming the top cross seal a pre-determined quantity of the product to be packaged is fed into the formed sachet which is then sealed at the top. (The seal temperature, pressure and dwell times will depend on the particular films being used. Seal widths may vary, depending on the particular application envisaged for the sachet).

A thermoforming process may also be used for rapid filled sachet production, wherein a film, usually a laminated film, is clamped across the width of a thermoformer and over a series of aluminium moulds which run the length of the machine. The film is heated to soften it into a semi-molten state. The air in each mould is then withdrawn through holes in the base of the mould, thus creating a zone of reduced pressure between the base and the mould. The atmospheric pressure on the film forces it onto the mould, where it cools sufficiently to retain its shape when removed from the mould. At this stage a pre-determined quantity of the product to be packaged is dosed into the so-formed pockets. As the product-filled pockets index into the sealing die, they are covered by a top layer of film. Finally, in one systematic move a heat sealing unit hermetically seals the top and bottom films together.

The films of the invention can also, if necessary, include small quantities of other materials such as slip aids, colourants, wetting agents (surfactants), fillers (e.g. silica), waxes, and chelating agents (e.g. ethylene diamine tetraacetic acid EDTA).

The present invention is now illustrated by reference to the following examples. Unless otherwise specified all parts, percentages and ratios are on a weight basis.

In the examples the following abbreviations are used :

25	BA	:	n-butyl acrylate
	EA	:	ethyl acrylate
	MMA	:	methyl methacrylate
	AA	:	acrylic acid
	MAA	:	methacrylic acid
30	Mw	:	weight average molecular weight.

Examples 1 to 17

Preparation of polymers

The following general procedure is used to make hard and soft copolymers for use in the invention.

A reactor is charged with 770.30g of water followed by 5.58g of a sulphonated nonylphenol ethoxylate (surfactant) and 3.18g of tertiary butyl-hydroperoxide (initiator). While creating a nitrogen atmosphere in the reactor, the temperature is brought to 82 ± 2°C and kept there during the whole polymerisation process. When the polymerisation temperature is reached an emulsified first feed (see Table 1a) is fed in during 90

minutes; after this a second feed (see Table 1b) is fed during 15 minutes. After completion of the feeds the reactor and its contents are cooled to room temperature. The result is an aqueous polymer latex (emulsion).

5 Table 1a : Composition of first feed

Water	248.65g
Sulphonated nonylphenol ethoxylate	8.37g
Iso-ascorbic acid	1.58g
3-mercaptopropionic acid *	3.17g
10 Monomers (see Table 2)	<u>633.75g</u>
	895.52g

* This amount is changed when different molecular weights are required.

15 Table 1b : Composition of second feed

Water	71.81g
Iso-ascorbic acid	0.63g
Ammonia (12½%)	<u>3.00g</u>
	75.44g

20

Polymer A : hard polymer

This polymer is prepared by the above described procedure without any changes. The composition of the monomer system used to make this polymer is shown in Table 2. The calculated Tg of this polymer is 52°C and the weight average molecular weight is about 50000. To make a clear solution of polymer A in water, 100g of the aqueous emulsion are blended with 24.14g of a 10% (by weight) sodium hydroxide solution and 97.73g of water. The obtained solution has a solids content of 17.5%.

Polymer B : soft polymer

30 This polymer is prepared by the above described procedure with the exception that 1.5g of 3-mercaptopropionic acid is used. The composition of the monomer system used to make this polymer is shown in Table 2. The calculated Tg of this polymer is -1°C and the weight average molecular weight is about 130000. To make a clear solution of polymer B in water, 100g of the aqueous emulsion are blended with 24.20g of a 10% (by weight) sodium hydroxide solution and 97.69g of water. The obtained solution has a solids content of 17.5%.

Polymer C : soft polymer

40 This polymer is prepared as for polymer B apart from the different levels of monomers used, shown in Table 2. The calculated Tg of this polymer is -1°C and the

weight average molecular weight is about 130000. To make a clear solution of polymer C in water, 100g of the aqueous emulsion are blended with 22.18g of a 10% (by weight) sodium hydroxide solution and 99.08g of water. The obtained solution has a solids content of 17.5%.

5

Polymer D : soft polymer

This polymer is prepared by the above described procedure. The amount of 3-mercaptopropionic acid used is 2.22g. The composition of the monomer system used to make the polymer is shown in Table 2. The calculated Tg is -1°C and the weight average molecular weight is about 100,000. To make a clear solution of polymer D in water, 100g of the aqueous emulsion are blended with 24.90g of a 10% (by weight) sodium hydroxide solution and 216.04g of water. The obtained solution has a solids content of 11.4%.

10

15

Polymer E : hard polymer

This polymer is prepared by the above described procedure. The composition of the monomer system used to make this polymer is shown in Table 2. The calculated Tg of this polymer is 55°C and the weight average molecular weight is about 50000. A clear solution of this polymer is made by adding 22.75g sodium hydroxide solution and 210.67g of water to 100g of aqueous emulsion. The obtained solution has a solids content of 11.6%.

20

Table 2 : Compositions of monomer systems used to make polymers A to E

	A	B	C	D	E
25 BA	-	35.6	31.8	36.3	-
EA	31.2	30.4	35.2	29.5	32.5
MMA	56.8	22.0	22.0	22.2	55.1
AA	12.0	12.0	11.0	12.0	6.0
MAA	-	-	-	-	6.0

30

Table 3 : Properties of polymers A to E

	<u>Tg°C (calc)</u>	<u>Mw</u>
35 A (hard)	52	50000
B (soft)	-1	130000
C (soft)	-1	130000
D (soft)	-1	100000
E (hard)	55	50000

40

Preparation of Films

Films were cast from solutions containing only copolymers A, B,C, D and E (Examples 1,15,16,17 and 2 respectively), solutions containing varying ratios of A/B (Examples 3 to 6), A/C (Examples 7 to 10), and E/D (Examples 11 to 14). The blend solutions were made by blending clear solutions of the two polymers (made as described above). Films for Examples 1,3 to 10, and 16, 17 were cast using a 800 μ m applicator bar (estimated to provide a dry film thickness of about 160 μ m) on release paper and dried for 1 hour at 80°C and then for 1 hour at 115°C. Films for Examples 2, 11 to 14 and 17 were prepared by drying the aqueous solutions in polyethylene lids for 1½ hours at 105°C (giving films of dry thickness ca 180 μ m). All the films were found to be completely soluble in cold water, although they dissolved at different rates; those with blend ratios according to the invention dissolved quickly at a rate acceptable for sachets.

Determination of Flexibility
The 180° bend test was used to determine whether the films made of the blends possess sufficient flexibility to be used in sachets. A film passes the 180° bend test when it does not crack or turn white in the bend when it is bent through 180°.

Table 4 : Results of 180°C bend test

<u>Example</u>	<u>Polymers</u>	<u>Ratio of</u>	<u>Flexibility</u>
<u>No.</u>	<u>in Blend</u>	<u>Polymers</u> <u>(hard/soft)</u>	<u>(180° bend test)*</u>
5			
1	A/-	100/-	-
2	E/-	100/-	-
3	A/B	50/50	-
10	A/B	40/60	-
4	A/B	30/70	+
5	A/B	20/80	+
6	A/B	50/50	-
7	A/C	40/60	-
8	A/C	30/70	+
15	A/C	20/80	+
9	E/D	50/50	-
10	E/D	40/60	-
11	E/D	30/70	±
12	E/D	20/80	+
13	-/B	-/100	+
20	-/C	-/100	+
14	-/D	-/100	+
15			
16			
17			

25 * + : passes test

- : fails test

± : on borderline of passing test

Examples 18 to 22

30 Further films were cast from a solution containing only copolymer B (Example 18) and solutions containing varying ratios of A/B (Examples 19 to 22) by casting the solution on release paper and drying for 1 hour at 80°C followed by 1 hour at 115°C (as described above for Examples 1,3 to 10, and 16, 17).

35 Determination of block resistance

Block resistance is tested by placing two free films on top of each other and then applying a pressure of 1kgcm^{-2} at the interface. This pressure is maintained for 4 hours at a temperature of 50°C. If after this period the two films do not stick, the film is rated as having passed the test for block resistance.

Table 5 : Results of block resistance test

	<u>Example No.</u>	<u>Polymers in Blend</u>	<u>Ratio of Polymers (hard/soft)</u>	<u>Block Resistance*</u>
5	18	-/B	-/100	-
	19	A/B	10/90	±
	20	A/B	20/80	+
10	21	A/B	30/70	+
	22	A/B	40/60	+

* + : passes test

- : fails test

15 ± : on borderline of passing test

It will be observed from the above-described flexibility and block resistance tests that blends having a ratio of soft/hard polymer below about 65/35 will tend to be too inflexible, while blends having a ratio of soft/hard polymers above 90/10 will tend to have insufficient block resistance (even though acceptably flexible).

Example 19

In this example an invention sachet containing a herbicide formulation was prepared.

25 A clear aqueous solution as used for Example 5 (i.e. a 30/70 blend of polymers A and B) was used for preparing films by coating onto the flame-treated side of polypropylene film (OPP 28MB250, ex Mobil) using a 400 Tm applicator bar, drying for 24 hours at room temperature, then for 1 hour at 80°C and then a further 1 hour at 115°C. The resulting films were peeled from the polypropylene backing and gave film thickness between 70-80 Tm.

30 The heat sealing conditions were determined. The heat seal threshold of 100g/inch was found to be reached at a temperature of 120°C, and a heat seal temperature window between 120°C and 150°C, for a dwell time of about 3 seconds.

35 A rectangular piece of film as prepared above of dimensions 220x90 mm was folded lengthwise to form an open sachet of dimensions 110x90 mm by heat sealing along the two side walls. The resultant seals were strong, yet soluble in cold water (20°C).

40 The open sachet was filled with 50g of a non aqueous, selective herbicide formulation, fluazifop-P-butyl gel (prepared according to the procedure described in Example 14 of patent application WO96/03871, entitled "Gel Formulation"). The top

opening of the sachet was then sealed. The gel-containing sachet was placed in a polyethylene outer pack which was sealed and stored under ambient conditions for 1 hour. The sachet showed no signs of leakage and the formulation remained contained.

5 The sachet was then added to 4.5 litres of tap water contained in a 5 litre glass beaker and stirred with a magnetic stirrer bar. The resulting dispersion was stirred at 600rpm for 10 minutes. A uniform emulsion was obtained, which on filtration through a 150 Tm sieve passed through with no blockage. A small amount of white residue remained on the mesh.

10 Example 20

A further invention sachet containing a herbicide formulation was prepared in this example.

15 A rectangular piece of film as prepared in Example 19 of dimensions 200x70 mm was folded lengthwise to form an open sachet of dimensions 100x70 mm, by heat sealing along the two side walls. The resultant seals were strong, yet soluble in cold water (20°C).

20 The open sachet was filled with 30g of an aqueous, nonselective herbicide concentrate of sulfosate (sulphosate: 800g, made up to 1 litre with water). The top opening of the sachet was then sealed. The liquid-containing sachet was placed in a polyethylene outer pack which was sealed and stored under ambient conditions for 24 hours. The sachet showed no signs of leakage and the formulation remained contained.

25 The sachet was then added to 4.5 litres of tap water contained in a 5 litre glass beaker and stirred with a magnetic stirrer bar. The resulting dispersion was stirred at 600rpm for 10 minutes. The sulfosate concentrate was released from the sachet as the film ruptured. On filtration, the resultant solution passed through a 150 Tm sieve with no blockage. A small quantity of white residue remained on the mesh.

CLAIMS

1. A flexible, water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film suitable for the enveloping material of a sachet, said film being comprised of a combination of the following polymer components S and H in which :
 - 5 S is defined as at least one acid-functional olefinic addition copolymer which is soft in character by virtue of having a $T_g \leq 20^{\circ}\text{C}$, and
 - H is defined as at least one acid-functional olefinic addition copolymer which is hard in character by virtue of having a $T_g \geq 40^{\circ}\text{C}$,
- 10 and wherein further the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35 and the acid-functionalities of S and H are at least partly neutralised such as to render the film water-soluble.
- 15 2. Film according to claim 1 wherein each copolymer of S and H is an acrylic polymer.
- 20 3. Film according to either claim 1 or claim 2 wherein the acid-functionality of each copolymer of S and H is derived from acid-functional olefinically unsaturated monomer(s) used in their preparation having acid groups selected from carboxyl and sulphonic acid groups, preferably carboxylic acid groups.
- 25 4. Film according to claim 3 wherein said acid-functional monomer(s) is (are) selected from acrylic and, methacrylic acid, α -carboxy-ethylacrylate, itaconic acid, maleic acid, and fumaric acid, and preferably from acrylic acid and methacrylic acid.
- 30 5. Film according to any one of the preceding claims wherein the acid-functionality of each copolymer of S and H is derived from olefinically unsaturated acid-functional monomer(s) used in the preparation thereof, said acid monomer(s) being employed in each case in an amount within the range of from 5 to 40 weight % based on the total weight of the monomers used for the preparation, preferably from 8 to 15 weight %.
- 35 6. Film according to any one of the preceding claims wherein said film is soluble in water at temperatures of $\leq 35^{\circ}\text{C}$, preferably within the range of from 5 to 35°C .
- 40 7. Film according to any one of the preceding claims where said film contains 0 to weight 15%, based on total polymer weight, of plasticising material, more preferably 0 to 4 weight %.
8. Film according to any one of the preceding claims wherein 50 to 100% of the acid groups are in neutralised form, preferably 80 to 100%.

9. Film according to any one of the preceding claims wherein each copolymer of S and H includes, in addition to polymerised units of acid functional monomer(s), polymerised units of soft and hard comonomers so as to provide Tg's of respectively \leq 5 20°C and \geq 40°C, a soft comonomer being a monomer which when homopolymerised yields a homopolymer of Tg $< 0^\circ\text{C}$, and a hard comonomer being a monomer which when homopolymerised yields homopolymer of Tg $> 20^\circ\text{C}$, preferably $> 60^\circ\text{C}$.

10. Film according to claim 9 wherein in a copolymer of S, the amount of soft 10 comonomer(s) in the monomer composition used for polymerisation is \geq 40 weight %, preferably \geq 50 weight %, of the monomers used.

11. Film according to either claim 9 or claim 10, wherein the soft monomer(s) 15 employed for each copolymer of S and H is selected from one or more of primary and secondary C1-C18 (preferably C1-C8) alkyl acrylates, primary and secondary C5-C18 alkyl methacrylates, polyolefines, conjugated dienes, and polyoxyalkylene-containing olefinically unsaturated monomers.

12. A film according to claim 11, wherein the soft monomer(s) is selected from one or 20 more of primary and secondary C1-C4 alkyl acrylates, preferably being one or more of methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate and n-butyl acrylate.

13. A film according to any one of claims 9 to 12 wherein the hard monomer(s) 25 employed for each copolymer of S and H is selected from one or more of C1-C4 alkyl methacrylates, benzyl acrylate, benzyl methacrylate, vinyl chloride, vinyl acetate, acrylonitrile, methacrylonitrile, styrene, chlorostyrene, and I-methyl styrene, and preferably one or more of methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and sec-butyl methacrylate.

30 14. A film according to any one of claims 9 to 13 wherein a copolymer of S is derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid-functional monomer(s), soft monomer(s), and hard monomer(s):

35 acid-functional monomer(s): 5 to 40 wt. %, preferably 8 to 15 wt. %,
soft monomer(s): 40 to 85 wt. %, preferably 55 to 70 wt. %,
hard monomer(s): 5 to 50 wt. %, preferably 15 to 35 wt. %,

where the above amounts of soft and hard monomers exclude acid-functional monomers whether hard or soft.

15. Film according to any one of claims 9 to 14 wherein a copolymer of H is derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid functional monomer(s), soft monomer(s), and acid-functional monomer(s):

5

acid-functional monomer(s): 5 to 40 wt. %, preferably 8 to 15 wt. %

soft monomer(s): 0 to 50 wt. %, preferably 10 to 40 wt. %

hard monomer(s): 40 to 90 wt. %, preferably 50 to 80. wt. %

10

where the above levels of soft and hard monomers exclude acid-functional monomers whether hard or soft.

15

16. Film according to any one of the preceding claims wherein each copolymer of S and H is prepared from a combination of monomers, which may be the same or different, selected from the following combinations: acrylic acid/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/methyl methacrylate; methacrylic acid/ethyl acrylate/n-butylacrylate/methyl methacrylate; acrylic acid/methacrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; and acrylic acid/methacrylic acid/ethyl acrylate/methyl methacrylate.

20

17. Film according to any one of the preceding claims wherein said at least partial neutralisation of the acid-functionalities in S and H has been effected with a non-volatile base, preferably NaOH, KOH, LiOH or a non-volatile aliphatic tertiary amine.

25

18. Film according to claim 17 wherein the amount of permanent base used for neutralisation has been in excess of that required for the neutralisation of all the acid-functional groups in S and H so that the film contains residual base from said neutralisation, preferably being present in an amount of up to 20 weight % based on the weight of the film.

30

19. Film according to any one of the preceding claims wherein the weight ratio of S to H is within the range of from 85/15 to 70/30.

35

20. Film according to any one of the preceding claims, wherein a soft copolymer of S has Tg within the range of from -20 to 20°C, preferably from -10 to 10°C.

21. Film according to any one of the preceding claims, wherein a hard copolymer of H has Tg within the range of from 40 to 90°C, preferably from 50 to 80°C.

22. Film according to any one of the preceding claims wherein the weight average molecular weight of a soft polymer of S is \leq 300,000, preferably being in the range of from 50,000 to 300,000.

5 23. Film according to any one of the preceding claims wherein the weight average molecular weight of a hard polymer of H is within the range of from 10,000 to 500,000, preferably from 30,000 to 200,000.

10 24. Polymer combination of polymer components S and H wherein S and H are as defined and are in combination according to any one of claims 1 to 23.

15 25. Polymer combination suitable for the provision of a flexible, water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film which is itself suitable for the enveloping material of a sachet, said polymer combination comprising a combination of the following polymer components S and H in which:

S is defined as at least one acid-functional olefinic addition copolymer which is soft in character by virtue of having a $T_g \geq 20^\circ\text{C}$, and

H is defined as at least one acid-functional olefinic addition copolymer which is hard in character by virtue of having a $T_g \geq 40^\circ\text{C}$,

20 and wherein the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35, and the acid-functionalities of S and H are either at least partly neutralised such as to render a film made from the polymer combination water-soluble, or are unneutralised or insufficiently neutralised to render a film made from the polymer combination water-soluble but are capable of being so at least partly neutralised such as to render a film made from the polymer combination water-soluble.

25 26. Aqueous polymer composition suitable for the provision of a film according to any one of claims 1 to 23 which composition comprises an aqueous solution or latex of the copolymers of S and H which are as defined and are in combination according to any one of claims 1 to 22 and which aqueous solution or latex has been derived from aqueous latices of the unneutralised copolymers.

30 27. Aqueous polymer composition suitable for the provision of a flexible, water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film suitable for the enveloping material of a sachet, said composition comprising an aqueous solution or latex of a combination of the following polymer components S and H in which:

S is defined as at least one acid-functional olefinic addition copolymer which is soft in character by virtue of having a $T_g \leq 20^\circ\text{C}$, and

H is defined as at least one acid-functional olefinic addition copolymer which is hard in character by virtue of having a $T_g \geq 40^\circ\text{C}$,

where the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35, and which aqueous solution or latex has been derived from aqueous latices of the unneutralised copolymers, and wherein in said composition the acid-functionalities of S and H are either at least partly neutralised such as to render a film made from the aqueous polymer composition water-soluble, or are unneutralised or insufficiently neutralised to render a film made from the aqueous polymer composition water-soluble but are capable of being so at least partly neutralised such as to render a film made from the aqueous polymer composition water-soluble.

5 28. Method of forming a film according to any one of claims 1 to 23 which comprises casting a composition according to either claim 26 or claim 27.

10 29. Sachet in which the enveloping film thereof comprises a film according to any one of claims 1 to 23.

15 30. Sachet according to claim 29 wherein the enveloping film thereof has a monolayer structure or a laminate structure.

20 31. Sachet according to claim 30 having a laminate structure, the outer film being a permanent base (preferably NaOH) - neutralised film according to any one of claims 1 to 23 which has residual base present therein as a result of the use of an excess of the permanent base over that required for neutralising all the acid groups, and the inner film being a volatile base (preferably ammonia) - neutralised film which is according to any one of claims 1 to 23 except that said volatile base has been caused or allowed to become released on film formation.

25 32. Sachet according to any one of claims 29 to 31 which is not fully sealed and has an opening(s) for receiving material to be packaged.

30 33. Sachet according to any one of claims 29 to claim 31 which is fully sealed and contains a packaged material.

35 34. Sachet according to claim 33 wherein the filled, fully sealed sachet has been made from film(s) using a vertical form-fill-seal process or a thermoforming process.

35 35. Sachet according to either claim 33 or claim 34 wherein the packaged material is in the form of a water-based composition.

40 36. Sachet according to any one of claims 33 to 35 wherein the packaged material is an agrochemical composition.

37. Sachet according to claim 36 wherein the packaged agrochemical composition is an insecticide, herbicide, fungicide, acaricide, or nematocide composition.

5 38. Sachet according to either claim 36 or claim 37 wherein the packaged agrochemical composition in the form of a particulate solid, a thickened liquid, or a gel.

39. Sachet according to any one of claims 33 to 35 wherein the packaged material is a laundry care composition.

10 40. Sachet according to any one of claims 33 to 35 wherein the packaged material is a dyestuff, a laundry item(s), a biocide, an industrial or home cleaner, or a public health product.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/GB 96/01264

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/18 B65D65/46 C08L33/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J B65D C08L C09D C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 576 128 (ROHM & HAAS) 29 December 1993 see claims 1-4 ---	24-27
X	DE,A,19 36 830 (RESART-IHM AG) 11 February 1971 see page 6, paragraph 3 - page 7 see page 1, paragraph 1 - paragraph 4 -----	1,24-28

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

21 August 1996

Date of mailing of the international search report

16.09.96

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/01264

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DE-A-1936830	11-02-71	NONE	

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